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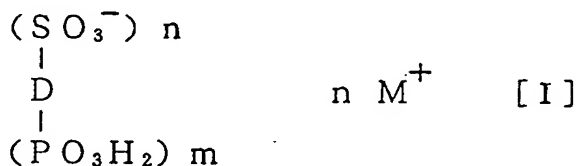
**EUROPEAN PATENT APPLICATION**

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(54) Salt-forming azodyes, their concentrated liquid compositions and ink compositions containing them.

(57) The present invention provides a novel salt-forming type dye represented by the formula:

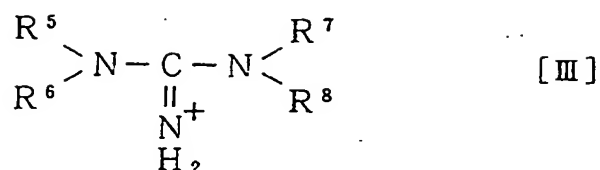


[wherein D is a residue of a monoazo or disazo dye, m is an integer of 1 to 3, n is an integer of 1 to 4, and M<sup>+</sup> is a cation selected from the group consisting of cations represented by the formulas:

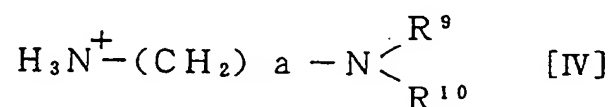


(wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are the same or different and indicate hydrogen, an alkyl group, an alkoxyalkyl group, a cyclohexyl group, an aralkyl group or a hydroxyalkyl group, and at least one of R<sup>1</sup> to R<sup>4</sup> is a branched or non-branched alkyl, alkoxyalkyl, cycloalkyl, aralkyl or polyoxyalkylene group having not less than 4 carbon

atoms),



(wherein  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  are the same or different and indicate hydrogen, an alkyl group, or a substituted or non-substituted phenyl group, and at least one of  $\text{R}^5$  to  $\text{R}^8$  is a substituted or non-substituted phenyl group), and



(wherein  $\text{R}^9$  and  $\text{R}^{10}$  are the same or different and indicate hydrogen or an alkyl group,  $a$  is an integer of not less than 3, and both  $\text{R}^9$  and  $\text{R}^{10}$  are not hydrogen)], and a process for producing the same. A concentrated solution composition and an ink composition are also disclosed.

The present invention relates to a novel salt-forming type dye and a process for producing the same, and a concentrated solution composition and an ink composition containing the salt-forming type dye. Particularly, it relates to a novel oil-soluble salt-forming type dye which can be used e.g. for autograph ink, jet printing ink, stamp ink and printing ink. More particularly, it relates to an azo salt-forming type dye having excellent solubility to a hydrophilic organic solvent (e.g. alcohols and glycols).

Heretofore, as the autographic ink or jet printing ink used for recording on materials to be recorded (e.g. paper) solutions and dispersions in which various dyes or pigments are dissolved or dispersed has been employed.

A pigment-dispersed type ink has such an advantage that it is superior in durability (e.g. light resistance).

However, a dispersion processing in which the pigment is sufficiently dispersed in this ink is required in order to prevent the pigment from precipitating or aggregating with time.

On the other hand, an oil ink or aqueous ink in which the dye is dissolved is advantageously used in comparison with the pigment because no troublesome dispersion processing is required.

However, in this kind of the ink or dye concentrated solution, no denaturation or precipitation of the dye with time should occur.

As the dye which satisfies such a requirement, for example, a salt-forming type basic and acidic dye, that in which a basic dye is treated with a fatty acid, metal complex-containing dye having a water-soluble group (e.g. sulfonic group) and that in which an acidic dye is treated with an organic amine are known.

However, a conventional oil ink in which an oil-soluble or alcohol-soluble dye is dissolved in a polar organic solvent is denaturated by an environmental change (e.g. temperature, humidity change). Particularly, it is liable to absorb water from the atmosphere and is inferior in storage stability, which results in deterioration of quality of the product.

Further, as the method for preparing a liquid composition of an anion type dye (e.g. aqueous ink, recording solution for jet printing) various methods have been suggested. Among the anion type dye, a direct dye, particularly black dye is generally inferior in water solubility and these dyes have an amino group in a dye molecular structure without exception. Therefore, when a liquid composition of these dyes is stored for a long period of time, deterioration due to oxidation is caused, which results in increase of viscosity, decrease of concentration and formation of precipitation. Accordingly, the improvement of these disadvantages is requested.

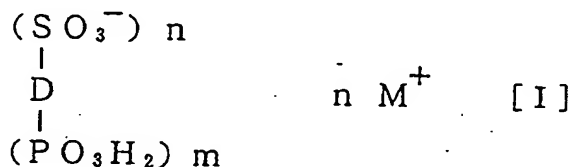
One object of the present invention is to provide a novel salt-forming dye having excellent solubility to a hydrophilic organic solvent (e.g. alcohols, glycols, etc.) or a mixture of a hydrophilic organic solvent and water (hereinafter, sometimes, referred to as "water-containing oil liquid solvent"), and a process for producing the same.

Another object of the present invention is to provide a high concentration liquid composition having excellent storage stability.

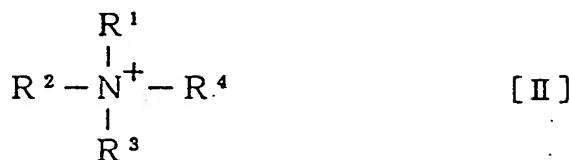
Still another object is to provide an aqueous/hydrophilic organic solvent type ink composition which is stable against absorption of water or environmental change.

These objects have been achieved on the basis of the finding that, by treating an azo water-soluble dye having a phosphonic acid group and sulfonic acid group in a dye molecular structure with a specific amine, a dye wherein the sulfonic acid group is preferentially or selectively salt-formed can be obtained and the salt-formed dye has excellent solubility to a hydrophilic organic solvent having low toxicity, or to an oil liquid solvent which may contain water.

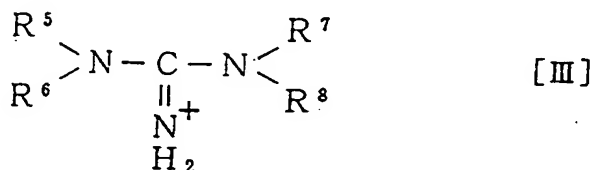
According to the present invention, there is provided a salt-forming type dye represented by the formula:



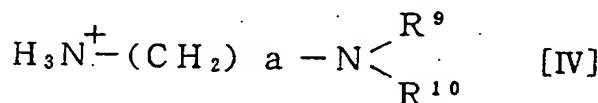
[wherein D is a residue of a monoazo or disazo dye, m is an integer of 1 to 3, n is an integer of 1 to 4, and M<sup>+</sup> is a cation selected from the group consisting of cations represented by the formulas:



(wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are the same or different and indicate hydrogen, an alkyl group, an alkoxyalkyl group, a cyclohexyl group, an aralkyl group or a hydroxyalkyl group, and at least one of  $\text{R}^1$  to  $\text{R}^4$  is a branched or non-branched alkyl, alkoxyalkyl, cycloalkyl, aralkyl or polyoxyalkylene group having not less than 4 carbon atoms),



(wherein  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$  and  $\text{R}^8$  are the same or different and indicate hydrogen, an alkyl group, or a substituted or non-substituted phenyl group, and at least one of  $\text{R}^5$  to  $\text{R}^8$  is a substituted or non-substituted phenyl group) and



(wherein  $\text{R}^9$  and  $\text{R}^{10}$  are the same or different and indicate hydrogen or an alkyl group,  $a$  is an integer of not less than 3, and both  $\text{R}^9$  and  $\text{R}^{10}$  are not hydrogen)] and a process for producing the same, and a concentrated solution composition and an ink composition containing the salt-forming type dye.

The salt-forming type dye of the present invention is an amine salt of an azo aqueous dye containing at least a phosphonic acid group and a sulfonic acid group (e.g. monoazo dye or disazo dye selected from an anion type acidic dye or direct dye). It can also be a polyazo dye (e.g. trisazo dye, etc.), however, solubility to a hydrophilic organic solvent or water-containing oil liquid medium becomes inferior, which results in deterioration of storage stability which is required for the autograph ink or jet printing ink. In the formula [I], numbers of the phosphonic acid group ( $m$ ) is preferably one in the case of the monoazo dye. When  $m$  is not less than 2, water solubility is too large and, therefore, solubility to the organic solvent becomes inferior. In the case of the disazo dye,  $m$  is 1 to 3. When  $m$  is not less than 4, water solubility is too large and, therefore, solubility to the organic solvent becomes inferior. Numbers of the sulfonic acid group which forms a salt with a cation  $\text{M}^+$  ( $n$ ) is 1 to 2 in the case of the monoazo dye. In the case of the disazo dye,  $n$  is 1 to 4. When  $n$  is not less than 5, oiliness becomes large and, therefore, solubility to the hydrophilic organic solvent or water-containing liquid medium becomes inferior. Preferably,  $n$  is 1 to 3. Further, the ratio of numbers of the phosphonic acid group ( $m$ ) to those of the sulfonic acid group ( $n$ ) is preferably 2:1 to 1:3.

In the formula [I], the cation  $\text{M}^+$  is selected from each cation represented by the above formulas [II] to [IV] and it may be also a mixture thereof. As to  $\text{R}^1$  to  $\text{R}^4$  in the formula [II], examples of the alkyl group include  $\text{C}_{1-18}$  alkyl groups, such as the methyl group, ethyl group, propyl group, amyl group, hexyl group, octyl group, nonyl group, dodecyl group, cetyl group, stearyl group and cyclohexyl group.

Examples of the alkoxyalkyl group generally contain 4 to 12 carbon atoms, including the 3-methoxypropyl group, 3-ethoxypropyl group, 3-butoxypropyl group, 3-octoxypropyl group, and 3-(2-ethylhexyl)propyl group and examples of polyoxyalkylene group include  $-(\text{CH}_2\text{CH}_2\text{O})_{2-6}-\text{H}$  and  $-(\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O})_{2-5}-\text{H}$ .

Examples of the aralkyl group include the benzyl group and  $\alpha,\alpha$ -dimethylbenzyl group. Examples of the hydroxyalkyl group generally contains 2 to 5 carbon atoms, including the 2-hydroxyethyl group, 3-hydroxypropyl group, 4-hydroxybutyl group and 2-hydroxypropyl group.  $\text{R}^1$  to  $\text{R}^4$  are the same or different and are

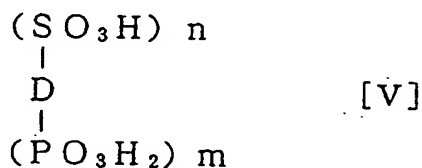
selected from these groups and H. Among  $R^1$  to  $R^4$ , at least one is a branched or non-branched alkyl, alkoxyalkyl, cyclohexyl, aralkyl or polyoxyalkylene group having not less than 4, preferably 5 to 12 carbon atoms.

As to  $R^5$  to  $R^6$  in the formula [III], examples of the alkyl group include those described as to the above  $R^1$  to  $R^4$ . As the substituted or non-substituted phenyl group, for example, there is a  $C_6$ -8 phenyl group and examples thereof include the phenyl group, tolyl group and xylyl group.

$R^5$  to  $R^8$  are the same or different and are selected from these substituents and H. Among  $R^5$  to  $R^8$ , at least one is a substituted or non-substituted phenyl group. The substituents include an alkyl group having 1 to 4 carbon atoms,

As to  $R^9$  and  $R^{10}$  in the formula [IV], examples of the alkyl group include those described as to the above  $R^1$  to  $R^4$ .  $R^9$  and  $R^{10}$  are the same or different and are selected from the above alkyl groups preferably having 1 to 12 carbon atoms and H, however, both of them are not H. In addition, a is an integer of not less than 3, preferably 3 to 6.

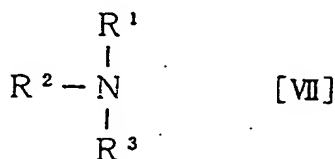
The salt-forming type dye [I] of the present invention is produced by reacting an azo water-soluble dye represented by the formula:



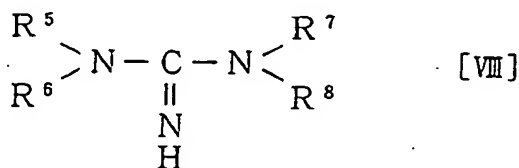
[wherein D, m and n are as defined above] with a cation forming agent selected from the group consisting of the compounds represented by the formulas:



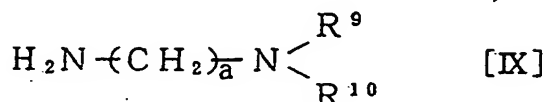
[wherein  $\text{Y}^-$  is an inorganic or organic anion, and  $\text{M}^+$  is as defined above],



[wherein  $\text{R}^1$  to  $\text{R}^3$  are as defined above],



[wherein  $\text{R}^5$  to  $\text{R}^8$  are as defined above], and



[wherein  $R^9$ ,  $R^{10}$  and  $a$  are as defined above].

In the formula [VI],  $Y^-$  is an inorganic or organic anion. Examples thereof include anion species in an inorganic acid salt (e.g.  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $SO_4^{2-}$ , etc.) and anion species in an organic acid salt (e.g.  $HCO_2^-$ ,  $CH_3CO_2^-$ , etc.). As the cation forming agent [VI], for example, there are those in which the compounds [VII] to [IX] as the other cation forming agent described below are neutralized with a corresponding inorganic or organic acid, or quaternized with a corresponding quaternizing agent (e.g. alkylating agent).

Examples of the compounds [VII] to [IX] as the other cation forming agent include aliphatic amines (e.g. dibutylamine, di-iso-butylamine, di-sec-butylamine, di-tert-butylamine, n-, iso-, sec-, tert-amylamine, hexylamine, pentylamine, octylamine, 2-ethylhexylamine, di-(2-ethylhexyl)amine and dodecylamine), alicyclic amines (e.g. cyclohexylamine and di-cyclohexylamine), alkoxyalkylamines (e.g. 3-ethoxypropylamine, di-(3-ethoxypropyl)amine, 3-butoxypropylamine, octoxypropylamine and 3-(2-ethylhexyloxy)propylamine), alkanol group-containing amines (e.g. N-cyclohexylethanolamine and N-dodecylimino-diethanol), diamines (e.g. dimethylaminopropylamine and dibutylaminopropylamine), guanidines (e.g. 1,3-diphenylguanidine, 1-o-tolylguanidine and di-o-tolylguanidine), and alkylene oxide addition amines having a molecular weight of 200 to 300 (e.g. ethylene oxide addition amine and long chain alkyl substituted-ethylene oxide addition amine).

One or more kinds of them may be used.

The above cation forming agent [VI] to [IX] may be preferably those which are low-volatile and contain one or more substituents having not less than 4 (particularly not less than 5) carbon atoms, a boiling point of which is not less than  $100^\circ C$ . When using a high-volatile cation forming agent, the resulting salt-forming type dye has not sufficient lipophilic nature, and it is not preferred.

In the reaction of the azo water-soluble dye with the cation forming agent, if necessary, other additives (e.g. urea and inorganic salts) may be added.

The reaction ratio of the azo water-soluble dye [V] to the cation forming agent may be a substantially stoichiometric amount. For example, the amount of the cation forming agent may be  $n$  to  $n+1$  moles based on 1 mole of the azo water soluble dye. The reaction may be conducted by a usual method, for example, by mixing the azo water soluble dye [V] with the cation forming agent with stirring at  $0$  to  $40^\circ C$  for 2 to 5 hours. Then, the mixture is subjected to a normal after-treatment [e.g. pH is adjusted to weak acidic (pH 4 to 7)], filtered, washed and dried to obtain a salt-forming type dye [I] of the present invention.

In the present invention, by using the above salt-forming type dye [I] thus obtained, it's concentrated solution composition, that is, a concentrated solution composition containing 15 to 35 % by weight of a salt-forming type dye and 75 to 85 % by weight of a hydrophilic organic solvent or a hydrophilic organic solvent having a water content of not more than 50 % can be prepared. As the hydrophilic organic solvent which can be used in the concentrated solution composition of the present invention, for example, there are monovalent alcohols (e.g. lower alcohols such as ethanol, n-propyl alcohol, iso-propanol, n-butanol and diacetone alcohol; monoalkyl ethers of diols such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monoethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether and dipropylene glycol monoethyl ether; monoacetates of diols such as ethylene glycol monoacetate and propylene glycol monoacetate; benzyl alcohol; and cyclohexanol), divalent alcohols (e.g. glycols such as ethylene glycol, diethylene glycol, trimethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, propylene glycol and butanediol), and trivalent alcohols (e.g. glycerine, trimethylolpropane and 1,2,6-hexanetriol). As the other hydrophilic organic solvent, for example, there are dioxane, 2-pyrrolidone, methyl lactate, ethyl lactate and butyl lactate and one or more kinds of them can be used. Preferably, low toxic or non-toxic compounds such as ethanol, propanol, propylene glycol monoalkyl ethers and lactic esters may be used.

Further, the above hydrophilic organic solvent may contain water. The water content is not more than 50 % by weight, preferably 20 % by weight. When the water content exceeds 50 % by weight, solubility and stability with time are deteriorated, and it is not preferred.

The salt-forming type dye represented by the formula [I] is dissolved in the above hydrophilic organic solvent and the solution is filtered, and then the dye concentration is adjusted to 15 to 35 % by weight to obtain a concentrated solution composition of the present invention. In this case, if necessary, additives (e.g. antiseptics and nonionic surfactant) may be added in a small amount.

In the concentrated solution composition of the present invention, pH adjustment is not particularly required and it is possible to store at a neutral state for a long period of time. Further, when pH is adjusted to 8 or more (e.g. with sodium hydroxide or lithium hydroxide) the cation forming agent is liberated, and it is not preferred.

Further, in the present invention, the ink composition containing the salt-forming type dye represented by the formula [I] of the present invention can be prepared. It is preferred that the ink composition of the present invention contains 1 to 30 % by weight of a salt-forming type dye [I] of the present invention, not

less than 60 % by weight of a hydrophilic organic solvent which may contain water described above and 5 to 10 % by weight of a resin, based on the total weight of the ink composition. The amount of the salt-forming type dye [I] varies depending on the application of the ink and is not specifically limited, and it may be 15 to 25 % by weight for a ball point pen, 5 to 15 % by weight for marking pen and 3 to 10 % by weight for ink-jet recording.

Further, by using the above concentrated solution composition of the present invention and, if necessary, adjusting the concentration it is possible to obtain the ink composition of the present invention.

The resin which can be suitably used in the ink composition of the present invention may be those which are normally used in the ink composition, for example, a water-soluble or alcohol-soluble resin. Example thereof include lower condensates of vinyl pyrrolidone, water-soluble alkyd resins, water-soluble acrylic resin, alcohol-soluble phenol resins, acrylic resins, styrene maleic resins and ketone resins.

As is described above, the salt-forming type dye of the present invention has the following advantages:

(1) Since it has free phosphonic acid group, affinity to a hydrophilic organic solvent and water-containing oil solution solvent is large;

(2) Since a water-soluble sulfonic acid group forms a salt with a specific amine, lipophilic nature is enhanced, which results in remarkable improvement of solubility to a hydrophilic organic solvent (e.g. alcohols and glycols); and

(3) Since the balance between the phosphonic acid group and amine sulfonate salt in the dye molecular structure is excellent, it is superior in matching with a water-containing oil solution solvent.

Further, the concentrated solution composition and ink composition of the present invention have also the following advantages:

(1) They show surprisingly high solubility to a solution solvent wherein the ratio of water to hydrophilic organic solvent is not more than 1 and are superior in storage stability;

(2) The dye is not denatured or precipitated according to environmental change (e.g. temperature, humidity change) and they are superior in stability with time;

(3) Since they are superior in solubility in a neutral solution solvent, corrosion of the part of a vessel which are in contact with the solution is not enhanced; and

(4) Since a low toxic organic solvent can be used, they are superior in acceptability to the human body.

The following Examples and Comparative Examples further illustrate the present invention in detail but are not construed to limit the scope thereof. In the Examples and Comparative Examples, all "parts" are by weight unless otherwise stated.

#### Example 1

##### Production of salt-forming type dye

3-Aminophenylphosphonic acid (17.3 parts) was diazotized by a conventional method and this was added to an aqueous alkali solution of 1,7-Cleve's acid (22.3 parts), followed by coupling at pH 8 to 9. The mixture was subjected to an acid salting-out treatment to precipitate a monoazo compound, which was dispersed in aqueous hydrochloric acid to diazotize it at 30 to 40 °C. Then, this diazo solution was added to a sodium carbonate alkali solution of 2R acid (2-amino-8-naphthol-3,6-disulphonic acid, 34 parts), followed by coupling at pH 8.5 to 9.0 and further precision filtration. To this was added 1,3-diphenylguanidine (60 parts) dissolved in aqueous acetic acid and the mixture was stirred at 0 to 5 °C for 2 hours, and pH was adjusted to weak acidic. Then, it was filtered, washed and dried to obtain a black dye (Black No.4, 65 parts) shown in Table 1. Further, its solubility is also shown in Table 1. In Table 1, P is  $-PO(OH)_2$ , S is  $-SO_3^-$  and a cation  $M^+$  which forms a salt with  $-SO_3^-$  is shown in the form of free amine. It is the same with Figs 2 and 3.

#### Examples 2 to 8

According to the same manner as that described in Example 1 except that the water-soluble dye (Black No.4) and 1,3-diphenylguanidine of Example 1 were respectively changed to the water-soluble dye and amine shown in Table 1, black salt-forming type dyes of Black Nos.1 to 3 (Examples 2 to 4) and Nos.5 to 8 (Examples 5 to 8) were obtained.

#### Example 9

3-Aminophenylphosphonic acid (17.3 parts) was diazotized by a conventional method and this was

added to an aqueous alkali solution of aniline- $\omega$ -sulfonic acid (21 parts), followed by coupling. By adjusting pH to strong alkali,  $\text{-NHCH}_2\text{SO}_3\text{Na}$  was changed to an amino group. The mixture was subjected to an acid salting-out treatment to precipitate a monoazo compound, which was dispersed in aqueous hydrochloric acid to diazotize it at 10 to 20°C. Then, this diazo solution was added to a sodium carbonate alkali solution of G acid (2-naphthol-6,8-disulfonic acid, 33 parts), followed by coupling at pH 8 to 8.5 and further precision filtration. To this was added di-(2-ethylhexyl)amine (48 parts) and the mixture was stirred at 10 to 20°C for 3 hours, and pH was adjusted to weak acidic. Then, it was filtered, washed and dried to obtain a red dye (Red No.1, 70 parts) shown in Table 2 described below.

#### Examples 10 to 12

According to the same manner as that described in Example 9 except that the water soluble dye (Red No.1) and di-(2-ethylhexyl)amine were respectively changed to the water-soluble dye and amine shown in Table 2 described below, red salt-forming type dyes of Red Nos.2 to 4 (Examples 10 to 12) were obtained.

#### Example 13

3-Aminophenylphosphonic acid (17.3 parts) was diazotized by a conventional method and this was added to an aqueous alkali solution of 1-amino-7-naphthol (16 parts), followed by acidic coupling at pH 3.5 to 4.0. A monoazo compound was precipitated and dispersed in aqueous hydrochloric acid to diazotize it at 5 to 15°C. Then, this diazo solution was added to an a sodium carbonate alkali solution of H acid (1-amino-8-naphthol-3,6-disulfonic acid, 34 parts), followed by coupling at pH 8.5 to 9.0 and further precision filtration. To this was added polyoxydodecylamine (48 parts) dissolved in aqueous hydrochloric acid and the mixture was stirred at 0 to 5°C for 3 hours, and pH was adjusted to weak acidic. Then, it was filtered, washed and dried under vacuum to obtain a blue dye (Blue No.2, 80 parts) shown in Table 3 described below.

#### Examples 14 and 15

According to the same manner as that described in Example 13 except that the water-soluble dye and polyoxydodecylamine of Example 13 were respectively changed to the water-soluble dye and amine shown in Table 3, blue salt-forming type dyes of Blue Nos.1 and 3 (Examples 14 and 15) were obtained.

#### Comparative Example 1

3-Aminophenylphosphonic acid (17.3 parts, 0.1 moles) was diazotized by a conventional method and this was added to an aqueous alkali solution of 1-phenyl-3-methyl-5-pyrazolone (17.4 g, 0.1 moles), followed by coupling at pH 8 to 9. Then, pH was adjusted to 9 to 10 and a monoazo compound was completely dissolved, followed by precision filtration. To this was added 1,3-diphenylguanidine (21 g) dissolved in aqueous acetic acid and the mixture was stirred at 10 to 20°C for 2 hours, and pH was adjusted to weak acidic. Then, it was filtered, washed and dried to obtain a dye (Comparative Example No.1) shown in Table 4. Yield was measured and, as a result, it was 30 g. Yield of this product corresponded to a chemical equivalent of a monoazo compound before salt-forming.

#### Comparative Example 2

According to the same manner as that described in Comparative Example 1 except that 3-aminophenylphosphonic acid (17.3 g, 0.1 moles) used in Comparative Example 1 was changed to metanilic acid (16.7 g, 0.1 moles), 50 g of a yellow dye of Comparative Example No.2 was obtained. Yield of this product corresponded to a chemical equivalent of a salt-formed monoazo compound.

#### Comparative Examples 3 to 8

According to the same manner as that described in Comparative Example 1 except that the diazo component (3-aminophenylphosphonic acid, metanilic acid) and coupling component (1-phenyl-3-methyl-5-pyrazolone) used in Comparative Example 1 or 2 were respectively changed to the others, dyes of Comparative Example Nos.3 to 8 (Comparative Examples 3 to 8) were obtained.

Solubility of each dye of the above Comparative Examples is shown in Table 4, respectively.



Example 16Concentrated solution composition of the present invention

5 A salt-forming type dye (No.4, 30 parts) of the present invention was uniformly mixed and dissolved in propylene glycol (70 parts) at 40 ° C, followed by precision filtration to prepare a black solution composition having a dye concentration of 30 %. This solution composition (30 ml) was placed in a 50 ml glass sampler and stability with time of the solution composition was examined by an incubator (manufactured by Sanyo Denki K.K.). A test was conducted at a temperature range between -5 and 50 ° C and a repeating time of 60  
10 minutes for 3 months and, as a result, no precipitation and denaturation of the dye were observed.

Example 17

15	Components	Amounts (parts)
	Deionized water	10
	Propylene glycol	70
	Salt-forming type dye of the present invention (Red No.1)	20
20	Antiseptics	0.1

By uniformly mixing and dissolving the above components at 40 ° C, a red solution composition having a dye concentration of 20 % was prepared according to the same manner as that described in Example 16. Stability with time was examined and, as a result, no precipitation of the dye was observed, as is the same  
25 as Example 16.

Example 18

30	Components	Amounts (parts)
	Deionized water	10
	Ethyl alcohol	40
	Propylene glycol monoethyl ether	30
35	Salt-forming type dye of the present invention (Black No.4)	15
	Low polymerization vinyl pyrrolidone resin	5

The above components were uniformly mixed and dissolved at 60 ° C, followed by precision filtration to  
40 obtain a black ink composition. According to the same manner as that described in Example 16, stability with time was examined. As a result, no precipitation of the dye was observed.

Examples 19 to 33

45 According to the same manner as that described in Example 18, each ink composition (Examples 19 to 33) of the present invention having a formulation shown in Table 5 was prepared, respectively. These ink compositions were stable for at least 3 months and no precipitation was observed.

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Table 1 (Black dye)

Black	Structural formula (Water-soluble dye)	Amine (M)	Solubility (g/100ml)		
			Ethanol	Glycol ether	Water:Solvent =2:8
No. 1		3-Ethoxy- propylamine	3	10	15
No. 2		Octoxy- propylamine	5	15	10
No. 3		Cyclohexyl- amine	5	30	20
No. 4		1,3- diphenyl- guanidine	5	30	30

Table 1 (continued)

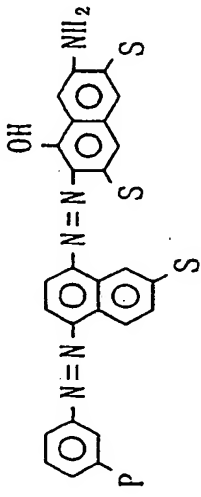
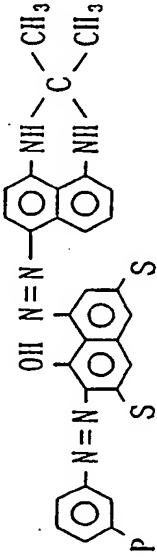
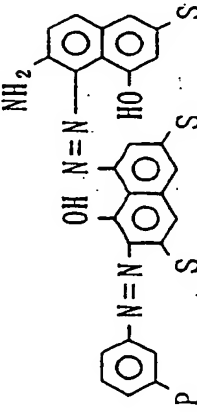
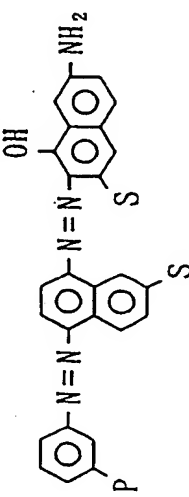
Black	Structural formula (Water-soluble dye)	Amine (M)	Solubility (g/100ml)		
			Ethanol	Glycol ether	Water:Solvent =2:8
No. 5		Polyoxy- dodecyl- amine	10	30	10
No. 6		Dicyclo- hexyl- amine	10	15	10
No. 7		2-Ethyl- hexyl- amine	3	20	30
No. 8		Octoxy- propyl- amine	8	30	20

Table 2 (Red dye)

Red	Structural formula (Water-soluble dye)	Amine (M)	Solubility (g/100ml)		
			Ethanol	Glycol ether	Water:Solvent =2:8
No. 1		Di-2-ethyl-hexyl-amine	10	20	30
No. 2		3-Butoxy-propyl-amine	8	25	30
No. 3		N-cyclohexyl-ethanol-amine	5	25	30

Table 2 (continued)

Red	Structural formula (Water-soluble dye)	Amine (M)	Solubility (g/100ml)		
			Ethanol	Glycol ether	Water:Solvent =2:8
No. 4		Dimethyl- amino- propyl- amine	3	30	30

Table 3 (Blue dye)

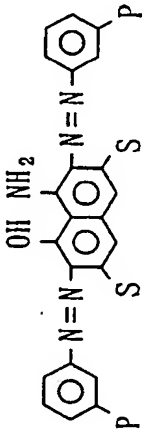
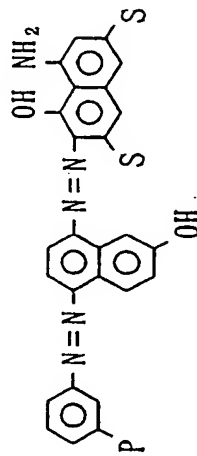
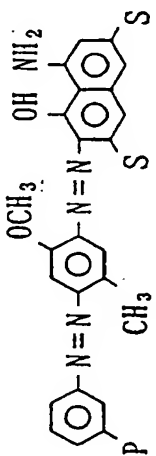
Blue	Structural formula (Water-soluble dye)	Amine (M)	Solubility (g/100ml)		
			Ethanol	Glycol ether	Water:Solvent =2:8
No. 1		L-amy1- amine	3	25	30
No. 2		Polyoxy- dodecyl- amine	5	25	30
No. 3		1-0-tolyl- guanidine	10	30	25

Table 4

Comp. Ex.	Structural formula	Solubility *1)			
		Water	Lower alcohol	Glycol ether	Water:Solvent =2:8
No. 1		D	D	C	C
No. 2	 +1,3-diphenyl- guanidine	D	C	B	C

## \*1) Evaluation:

A: dissolved in an amount of 10% or more

B: dissolved in an amount of 5~10%

C: dissolved in an amount of 5% or less

D: dissolved in an amount of 1% or less

Table 4 (continued)

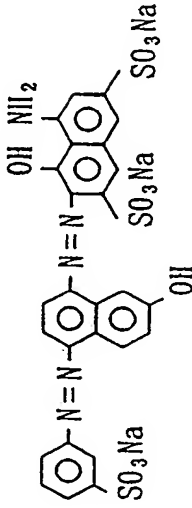
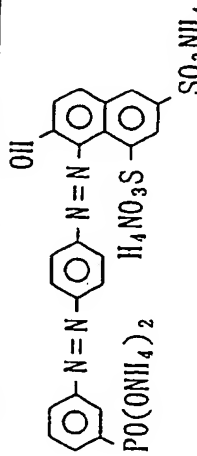
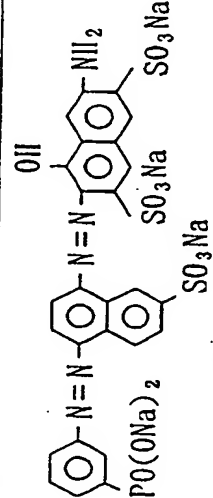
Comp. Ex.	Structural formula	Solubility *1)			
		Water	Lower alcohol	Glycol ether	Water:Solvent =2:8
No. 3		A	D	D	C
No. 4		A	D	C	C
No. 5		A	D	C	D



Table 4 (continued)

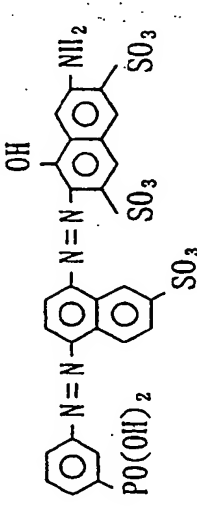
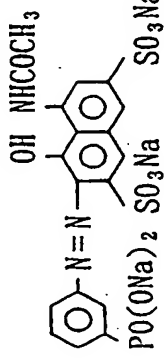
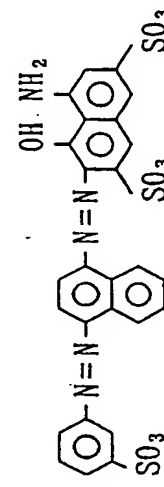
Comp. Ex.	Structural formula	Solubility *1)			
		Water	Lower alcohol	Glycol ether	Water:Solvent =2:8
No. 6	 $+ 3 \text{ H}_2\text{N} \begin{matrix} \text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{CH}_3 \end{matrix}$	C	C	B	C
No. 7	 $+ 3 \text{ H}_2\text{N} \begin{matrix} \text{CH}_2\text{CH}_3 \\ \text{CH}_2\text{CH}_3 \end{matrix}$	A	D	D	C
No. 8	 $+ 3 \text{ NH}_3\text{C}_{12}\text{H}_{25}$	D	C	B	D

Table 5

Example No.	Salt-formed dye	Water	Water-soluble organic solvent Alcohol	Glycols, etc.	Resin
19	Black No.1	10	Ethanol 40	PME 30	Low polymerization vinyl pyrrolidone 10
20	Black No.2	10	Ethanol 50	Ethyl lactate 20	Acrylic resin 10
21	Black No.3	10	Ethanol 10	PME 57	Arakyd resin 8
22	Black No.4	5	Ethanol 65	-	Low polymerization vinyl pyrrolidone 10
23	Black No.5	10	-	PG 62	Low polymerization vinyl pyrrolidone 8
24	Black No.6	-	Ethanol 18	PME 60	Phenol resin 10
25	Black No.7	20	-	DEG 70	Low polymerization vinyl pyrrolidone 5
26	Black No.8	-	Ethanol 65	Ethyl lactate 10	Ketone resin 10

Unit: % by weight

PME: Propylene glycol monomethyl ether

PG: Propylene glycol

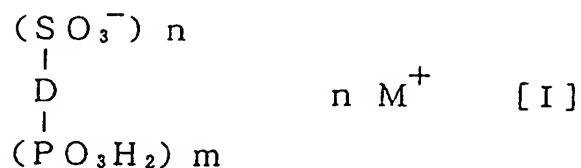
DEG: Diethylene glycol

Table 5 (continued)

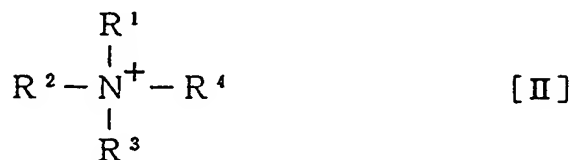
Example No.	Salt-formed dye	Water	Water-soluble organic solvent Alcohol	Glycols, etc.	Resin
27	Red No.1	-	Ethanol 70	Ethyl lactate 14	Phenol resin 8
28	Red No.2	10	Ethanol 25	PME 50	Acrylic resin 5
29	Red No.3	15	-	DEG 69	Low polymerization vinyl pyrrolidone 8
30	Red No.4	10	-	PG 77	Arakyd resin 5
31	Blue No.1	5	Ethanol 13	PME 70	Acrylic resin 5
32	Blue No.2	-	Ethanol 70	Ethyl lactate 15	Ketone resin 8
33	Blue No.3	10	-	PG 74	Low polymerization vinyl pyrrolidone 8

## Claims

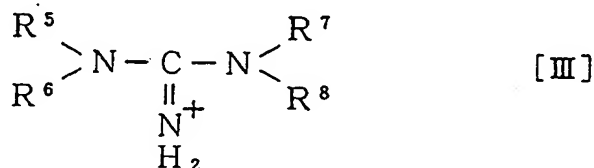
1. A salt-forming type dye represented by the formula;



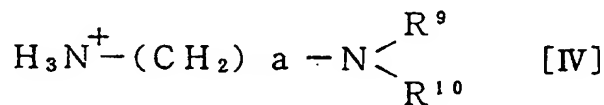
[wherein D is a residue of a monoazo or disazo dye, m is an integer of 1 to 3, n is an integer of 1 to 4, and M<sup>+</sup> is a cation selected from the group consisting of cations represented by the formulas:



(wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are the same or different and indicate hydrogen, an alkyl group, an alkoxyalkyl group, a cyclohexyl group, an aralkyl group or a hydroxyalkyl group, and at least one of R<sup>1</sup> to R<sup>4</sup> is a branched or non-branched alkyl, alkoxyalkyl, cycloalkyl, aralkyl or polyoxyalkylene group having not less than 4 carbon atoms),

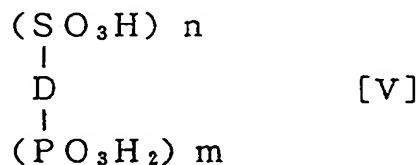


(wherein R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are the same or different and indicate hydrogen, an alkyl group, or a substituted or non-substituted phenyl group, and at least one of R<sup>5</sup> to R<sup>8</sup> is a substituted or non-substituted phenyl group), and

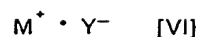


(wherein R<sup>9</sup> and R<sup>10</sup> are the same or different and indicate hydrogen or an alkyl group, a is an integer of not less than 3, and both R<sup>9</sup> and R<sup>10</sup> are not hydrogen).

2. A process for producing the salt-forming type dye according to claim 1, which comprises reacting a compound represented by the formula:



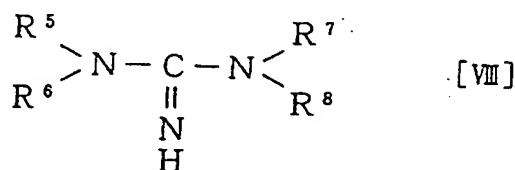
[wherein D, m and n are as defined above] with a cation forming agent selected from the group consisting of the compounds represented by the formulas:



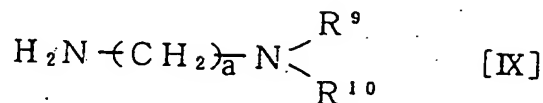
[wherein  $Y^-$  is an inorganic or organic anion, and  $M^+$  is as defined above],



[wherein  $R^1$  to  $R^3$  are as defined above],



[wherein  $R^5$  to  $R^8$  are as defined above], and



[wherein  $R^9$ ,  $R^{10}$  and  $a$  are as defined above].

3. A concentrated solution composition which comprises 15 to 35 % by weight of the salt-forming type dye according to claim 1 and 75 to 85 % by weight of a hydrophilic organic solvent or a hydrophilic solvent having a water content of not more than 50 % by weight.
4. An ink composition which comprises the salt-forming type dye according to claim 1, a hydrophilic organic solvent or a hydrophilic organic solvent having a water content of not more than 50 % by weight and a resin.
5. The concentrated solution composition according to claim 3, wherein the hydrophilic organic solvent is selected from the group consisting of alcohols, glycols and lactic esters.
6. The ink composition according to claim 4, wherein the hydrophilic organic solvent is selected from the group consisting of alcohols, glycols and lactic esters.
7. The ink composition which comprises the concentrated solution composition according to claim 3 or 5.



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## EUROPEAN SEARCH REPORT

Application Number

EP 92 10 6231

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 021 619 (ICI) * page 1, line 1 - page 7, line 22; examples 1-3 * * page 5, line 4 - line 12 *	1-4,5	C09B69/04 C09B69/00 C09D11/16 C09D11/18 C09D11/00
Y	DE-A-2 636 608 (BURLINGTON IND.) * page 2 * * page 3, line 24 - page 4, line 5 *	1,2	
Y	DE-A-2 006 517 (BASF) * page 2 *	1,2	
A	EP-A-0 049 338 (IBM) * page 3, line 1 - line 3; claims *	1-7	
A	GB-A-2 006 801 (ICI) * page 1, line 45 - line 50 *	1,2	
A	GB-A-2 007 265 (ICI) * page 1, line 68 - line 72; examples *	1,2	
A	GB-A-1 511 459 (BURLINGTON IND.) * page 1, line 12 - page 2, line 4 *	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	GB-A-1 491 595 (ICI) * page 4, line 31 - page 5, line 4; examples *	1,2	C09B C09D
A	EP-A-0 030 389 (SAKURA COLOR PRODUCTS CORP.) * claims *	1-7	
A	EP-A-0 347 803 (ORIENT CHEM. IND.) * the whole document *	1-7	
A	EP-A-0 241 413 (CIBA-GEIGY) * page 1, line 10 - page 2, line 10 * * page 5, line 5 - line 10 *	1	
A	EP-A-0 276 534 (CROMPTON & KNOWLES) * page 2 * * page 5, line 31 - line 45 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 JULY 1992	Examiner KETTERER M.
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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-1 941 105 (BAYER) * page 2, line 3 - page 5 *	1	
A	DE-C-533 871 (I. G. FARBEN) * the whole document *	1,2	
A	DE-C-469 179 (DU PONT DE NEMOURS) * the whole document *	1,2	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 17 JULY 1992	Examiner KETTERER M.	
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